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Two unique star-like [$Mn^{IV}Mn^{III}_2Ln^{III}$] clusters: magnetic relaxation phenomena

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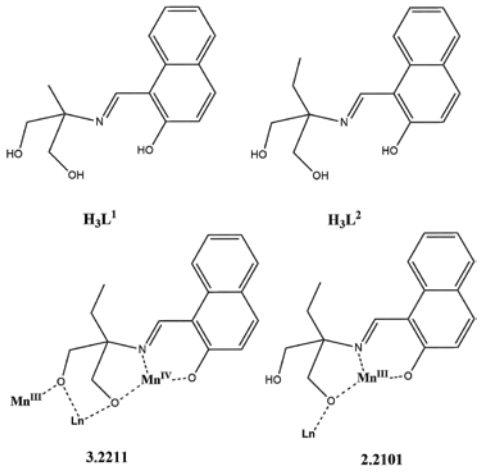
Employment of H_3L^2 (= 2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) in manganese-lanthanide cluster chemistry has led to the isolation of two new isostructural tetrametallic [$Mn^{III}_2Mn^{IV}Ln^{III}$] complexes (Ln = Gd, Dy), with the Dy analogue displaying temperature and frequency dependent out-of-phase signals, thus indicating possible single molecule magnetism behaviour.

The last decade has witnessed a major boost in the field of molecular magnetism. Since the discovery of the prototype single molecule magnet (SMM) [$Mn_{12}OAc$] that could retain its magnetization once magnetized at temperatures below ~3 K,[1] various significant achievements have been accomplished: i) in 2007 a hexanuclear [Mn^{III}_6] cluster was reported with an energy barrier for the re-orientation of the magnetization of U_{eff} = 86.4 K, breaking the record of U_{eff} = 60-64 K held by the prototype SMM for ~15 years,[2] ii) in 2009 a [Dy^{III}_4] cluster was reported elevating the energy barrier to 170 K,[3] iii) in 2011 Long *et al.* synthesized a radical-bridged [Dy^{III}_2] complex with a blocking temperature of 8.3 K and U_{eff} = 178 K,[4] while the terbium analogue displayed a blocking temperature of ~14 K and U_{eff} = 326 K,[5] iv) in 2013 Winpenny *et al.* reported polynuclear lanthanide alkoxide complexes with U_{eff} values higher than 800 K,[6] and v) very recently a number of pentagonal bipyramidal mononuclear Dy^{III} complexes have been reported with blocking temperatures reaching 20 K[7] and U_{eff} values > 1000 K.[8] From these recent benchmarks, it is apparent that the use of lanthanide ions in molecular magnetism has become a key element towards the improvement of the magnetic properties of discrete clusters and their potential technological applications as magnetic memory devices.

We previously reported the use of the naphthalene-based triol ligand 2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol, H_3L^1,[9] in Co(II/III), Ni(II) and Cu(II) chemistry,[10] and recently expanded our studies to mixed-metal Mn/Ln chemistry reporting a family of octanuclear [$Mn^{III}_6Ln^{III}_2$] complexes,[11] and two dodecanuclear [$Mn^{III}_6Ln^{III}_6$] clusters (Ln = Gd, Dy).[12] Herein, we present our efforts towards the use of H_3L^2 (=2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) in Mn/Ln cluster chemistry, and report the synthesis, structures and magnetic properties of two tetrametallic [$Mn^{IV}Mn^{III}_2Ln^{III}$] clusters (Ln = Gd, Dy).



Scheme 1. The structures of H_3L^1 and H_3L^2 (top), and the coordination modes of H_3L^2 in **1** and **2** using Harris notation (bottom).

From the reaction of $Mn(ClO_4)_2{\cdot}6H_2O$, $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Gd, Dy), H_3L^2 and NH_4SCN in 1:1:1:3 ratio in the presence of base, NEt_3, in MeOH we were able to isolate and characterize two new heterometallic tetranuclear clusters with the general formula $[Mn_3Ln(L^2)_2(HL^2)_2(naph)(NCS)(H_2O)(MeOH)_{1.8}](0.5NO_3)(0.5ClO_4){\cdot}1.8MeOH{\cdot}0.6H_2O$ (naph: naphthaldehyde; Ln: Gd, **1**·1.8MeOH·0.6H_2O; Dy, **2**·1.8MeOH·0.6H_2O). The structure of **1** was solved by single-crystal X-ray crystallography, while complex **2** is isostructural with **1** based on elemental analyses, IR spectra and powder XRD patterns (Figs S1 and S2). Cluster **1** crystallizes in the triclinic P-1 space group

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(Figure 1); its metallic core describes a central Gd^{III} ion bridged to three peripheral manganese centers *via* six μ-OR^- groups from the four deprotonated/partially-deprotonated naphthalene-triol ligands present in the structure. Two of the ligands are fully deprotonated, L^{3-}, adopting a 3.2211 coordination mode (Harris notation),[13] while the remaining two are partially deprotonated, HL^{2-}, with a 2.2101 binding mode. The lanthanide center completes its eight-coordinate sphere with a chelating naphthaldehyde group, arising upon the *in situ* breaking of the Schiff-base triol ligand. All three manganese centers are six-coordinate, completing their coordination environment with the presence of solvate molecules (for Mn2) and one terminal thiocyanate ligand (for Mn3). Mn2 and Mn3 are in the 3+ oxidation state as confirmed by bond-valence sum calculations [14] (BVS values: 3.14 and 3.06, for Mn2 and Mn3, respectively), with both of them adopting a *JT*-distorted octahedral geometry, while Mn1 is found in the 4+ oxidation level (BVS value: 3.94). The coordination sphere of the lanthanide center was found following SHAPE[15] analysis to be square antiprismatic (Table S1). The metallic cores of **1** and **2** have a star-like topology, which is extremely rare in Mn/Ln chemistry, with only two previous examples reported,[16] while this is the first case in which the 3d centers are found in a mixed-valent state.

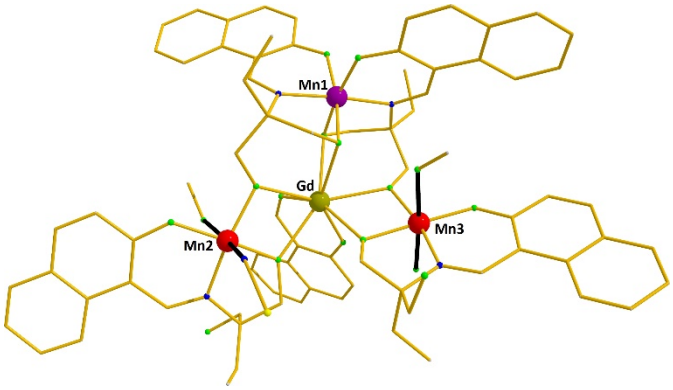

Figure 1. The molecular structure of the cation of **1**, highlighting the orientation of the two *Jahn-Teller* axis (bold line). Solvent molecules and H atoms are omitted for clarity. Color code: Mn^{IV}= purple, Mn^{III} = red, Gd^{III} = dark-yellow, O = green, S = yellow, N = blue, C = grey.

Variable temperature *dc* magnetic susceptibility data were collected for both complexes in the temperature range 5-300 K under an applied field of 0.1 T, and are plotted as $\chi_M T$ versus T plots in Figure 2. For **1**, the room temperature $\chi_M T$ value of 15.30 cm^3 K mol^{-1} is very close to the expected value of 15.75 cm^3 K mol^{-1} for two non-interacting Mn^{III} (with g = 2.0), one Mn^{IV} (g = 2.0) and one Gd^{III} ions (g = 2.00). Upon cooling the value of $\chi_M T$ remains almost unchanged until ~100 K, below which it decreases to a minimum value of 5.09 cm^3 K mol^{-1} at 5 K. For **2**, the room temperature $\chi_M T$ value of 21.75 cm^3 K mol^{-1} is very close to the expected value of 21.97 cm^3 K mol^{-1} for two non-interacting Mn^{III} (with g = 2.0), one Mn^{IV} (g = 2.0) and one Dy^{III} ions (S = 5/2, L = 5, J = 15/2, g_j = 4/3). Upon cooling the value of $\chi_M T$ remains fairly constant until ~120 K, below which it decreases to a final value of 12.01 cm^3 K mol^{-1} at 5 K.

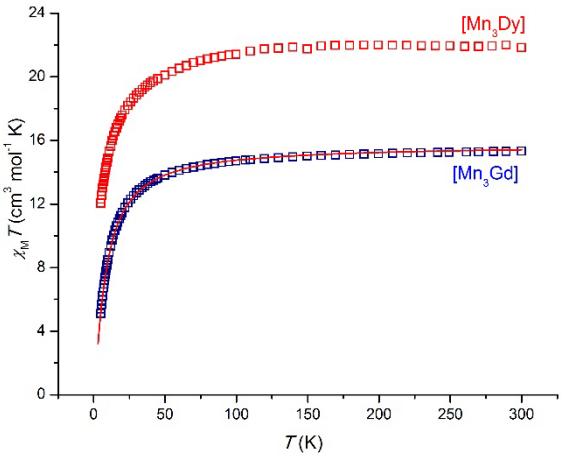

Figure 2. $\chi_M T$ *vs.* T plot for complexes **1** ([Mn_3Gd]) and **2** ([Mn_3Dy]) under an applied *dc* field of 0.1 T. The solid line represents a simulation of the magnetic susceptibility data for **1** (see text for details).

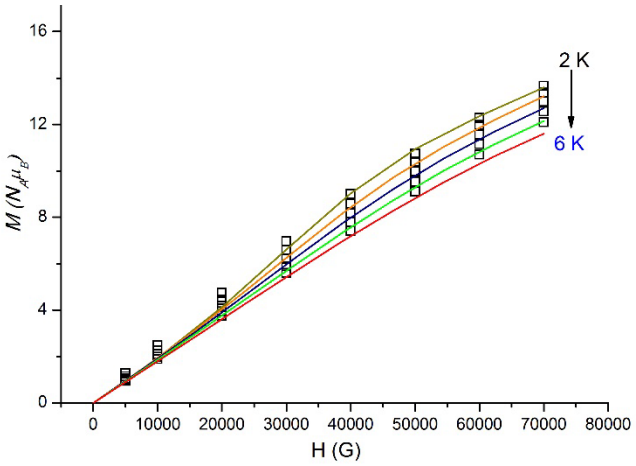

Figure 3. *M vs. H* plot for complex **1** ([Mn_3Gd]) in the 1 – 7 T and 2.0 – 6.0 K field and temperature range. The solid lines represent a simulation of the magnetization isotherms in the 2-6 K temperature range (see text for details).

In Figure 3, the magnetization data is presented for complex **1** as a *M vs. H* plot. We were able to successfully simulate both the magnetic susceptibility and magnetization data, assuming a 3-*J* model with: i) J_1 between Mn1-Mn2 and Mn1-Mn3, ii) J_2 between the trivalent Mn centers (Mn2-Mn3), and iii) J_3 between the Gd center and its peripheral manganese centers. Using the program PHI[17] and employing the Hamiltonian in eqn (1)

$$\hat{H} = -2J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3) - 2J_2(\hat{S}_2\cdot\hat{S}_3) - 2J_3(\hat{S}_1\cdot\hat{S}_4 + \hat{S}_2\cdot\hat{S}_4 + \hat{S}_3\cdot\hat{S}_4) \quad (1)$$

afforded the parameters J_1 = -0.52 cm^{-1}, J_2 = 0.12 cm^{-1}, J_3 = -0.36 cm^{-1}, $g_{Mn(IV),Mn(III),Gd(III)}$ = 2.00 . These parameters lead to a spin-frustrated system with a band of near degenerate S states of value S = 0, S = 1 and S = 2, all within ~1.5 cm^{-1}, as expected due to the very weak interactions present within the cluster. The magnitude and nature of parameters J_2 and J_3 are in agreement with the previously reported star-like [Mn^{III}_3Gd] complex ($J_{Mn(III)}$-

$_{Mn(III)}$ = 0.56 cm^{-1} *vs*. 0.12 cm^{-1} in **1**, $J_{Mn\text{-}Gd}$ = -0.23 cm^{-1} *vs*. -0.36 cm^{-1} in **1**),[16a] and the Mn-Gd interaction, J_3, also falls within the range for previously reported values.[18] It is worth noting that to avoid over-parameterization problems, we treated the system with only one Mn-Gd interaction, J_3. Given the expected small magnitude of both Mn^{III}-Gd and Mn^{IV}-Gd interactions due to the core-like nature of the 4*f* electrons, we chose not to distinguish between the two distinct interactions present in **1**.

Given the relatively large magnetic moment of cluster **2**, *ac* magnetic susceptibility measurements were performed on a polycrystalline of **2** in the 1.8-8 K range in zero applied *dc* field and a 3.5 G *ac* field oscillating at 200-1000 Hz frequency. The in-phase signal decreases upon decreasing temperature, indicating the presence of low-lying excited states with larger "*S*" values than the ground-state (Figure 4, top), while in addition frequency-dependent out-of-phase (χ_M'') "tails" are observed below ~3.7 K (Figure 4, bottom, and Fig. S3), suggesting possible single molecule magnetism behaviour. On the contrary, complex **1** displays no out-of-phase signals, clearly showing that the magnetic relaxation of cluster **2** is mainly due to the presence of the Dy^{III} center and not the Mn^{III} centers.

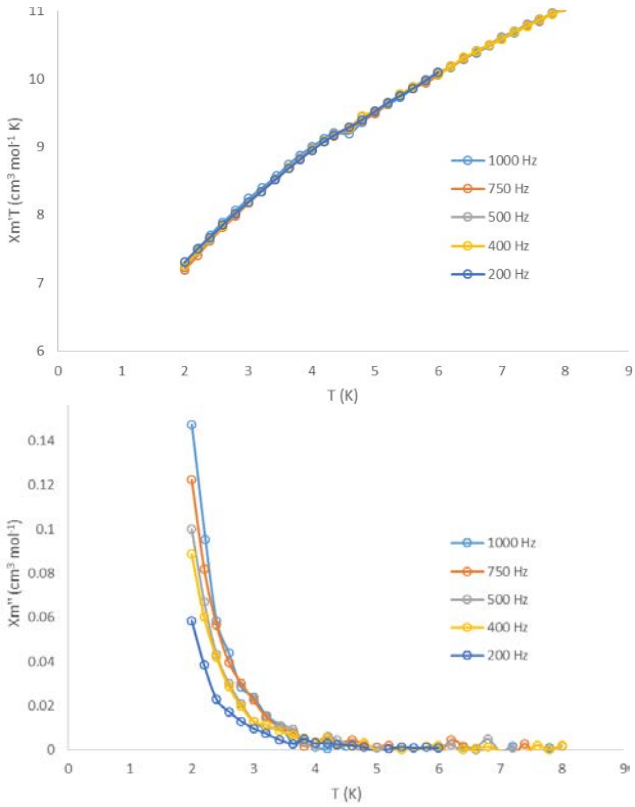

Figure 4. Plot of the in-phase χ_M'T (top) and out-of-phase χ_M'' signals (bottom) for **2** in *ac* susceptibility studies vs. *T* in a 3.5 G oscillating field at the indicated frequencies.

Conclusions

Two new heterometallic tetranuclear [$Mn^{IV}Mn^{III}_2$Ln] (Ln = Gd, Dy) star-like clusters have been synthesized with the use of the H_3L^2 (= 2-(β-naphthalideneamino)-2-hydroxyethyl-1-propanol) ligand in mixed-metal Mn/Ln chemistry. They represent the first examples of a mixed-valent Mn/Ln complex with a star-like topology, and the magnetic properties of the Dy analogue, **2**, suggest possible single molecule magnetism behaviour.

Acknowledgements

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Notes and references

§ Crystal data for **1**: ($C_{77.80}H_{80.4}GdMn_3N_5O_{16.8}S$)·0.5($ClO_4$)·0.5($NO_3$)·1.8($CH_3OH$) ·0.6($H_2O$), M = 1857.61, triclinic, space group P-1, a = 16.077(7) Å, b = 16.201(7) Å, c = 18.740(8) Å, α = 70.68(4)°, β = 84.13(4)°, γ = 68.67(3)°, V = 4290(3)Å^3 , Z = 2, T = 100 K, R1 (I > 2σ) = 0.064 and wR2 (all data) = 0.201 for 32407 reflections collected, 14826 observed reflections (I > 2σ(I)) of 21792 (Rint = 0.032) unique reflections and 1171 parameters, GOF = 1.07. CCDC reference number: 1470482.

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